VISIT…

29
Resorcinol Adhesives

A. Pizzi
Ecole Nationale Supérieure des Technologies et Industries du Bois, Université de Nancy I, Epinal, France

I. INTRODUCTION

Resorcinol–formaldehyde (RF), and phenol–resorcinol–formaldehyde (PRF) cold-setting adhesives are used primarily in the manufacture of structural, exterior-grade glulam fingerjoints, and other exterior timber structures. They produce bonds not only of high strength, but also of outstanding water and weather resistance when exposed to many climatic conditions [1,2]. PRF resins are prepared mainly by grafting resorcinol onto the active methylol groups of the low-condensation resols obtained by the reaction of phenol with formaldehyde. Resorcinol is the chemical species that gives to these adhesives their characteristic cold-setting behavior. At ambient temperature and on addition of a hardener, it provides accelerated and improved cross-linking not only to RF resins but also to the phenol–formaldehyde (PF) resins onto which resorcinol has been grafted by chemical reaction during resin manufacture. Resorcinol is an expensive chemical, produced in very few locations around the world (to date only three commercial plants are known to be operative: in the United States, Germany, and Japan), and its high price is the determining factor in the cost of RF and PRF adhesives. It is for this reason that the history of RF and PRF resins is closely interwoven, by necessity, with the search for a decrease in their resorcinol content, without loss of adhesive performance.

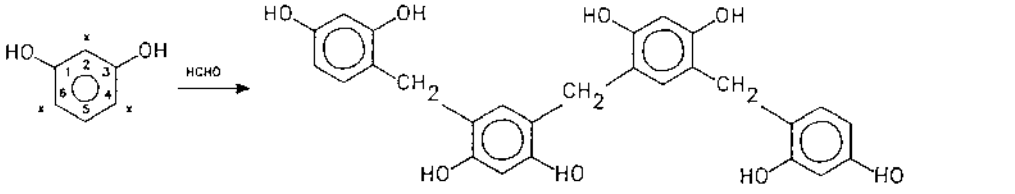
In the past decades, significant reductions in resorcinol content have been achieved: from pure RF resins, to PRF resins in which phenol and resorcinol were used in equal or comparable amounts, to the modern-day commercial resins for glulam and fingerjointing in which the percentage, by mass, of resorcinol on liquid resins is on the order of 15 to 18%. A step forward has also been the development and commercialization of the ''honeymoon'' fast-set system [3], either composed of just synthetic PRF resins or of a PRF resin coupled with the use of tannin extracts, which in certain countries are used to obtain PRFs of 8 to 9% resorcinol content without loss of performance and with some other advantages (such as gluing of high moisture content timber). This was a system improvement, not an advance on the basic formulation of PRF resins.

Copyright © 2003 by Taylor & Francis Group, LLC

II. CHEMISTRY OF RF RESINS

The same chemical mechanisms and driving forces presented for PF resins apply to resorcinol resins. Resorcinol reacts readily with formaldehyde to produce resins which harden at ambient temperatures if formaldehyde is added. The initial condensation reaction, in which A-stage liquid resins are formed, leads to the formation of linear condensates only when the resorcinol/formaldehyde molar ratio is approximately 1:1 [4]. This reflects the reactivity of the two main reactive sites (positions 4 and 6) of resorcinol [5]. However, reaction with the remaining reactive but sterically hindered site (2-position) between the hydroxyl functions also occurs [4]. In relation to the weights of RF condensates which are isolated and on a molar basis, the proportion of 4- plus 6-linkages relative to 2-linkages is 10.5:1. However, cognizance must be taken of the fact that the first mentioned pair represents two condensation sites relative to one. The difference in reactivity of the two types of sites (i.e., 4- or 6-position relative to the 2-position) is then 5:1 [4]. Linear components always appear to form in preference to branched components in A-stage resins [4]; that is, terminal attack leads to the preferential formation of linear rather than branched condensates. This fact can be attributed to:

1. The presence of two reactive nucleophilic centers on the terminal units, as opposed to single centers of doubly bound units already in the chain.
2. The greater steric hindrance of the available nucleophilic center (nearly always at the 2-position) of the doubly bound units as opposed to the lower steric hindrance of at least one of the nucleophilic centers of the terminal units (a 4- or 6-position always available). The former is less reactive as a result of the increased steric hindrance. The latter are more reactive.
3. The lower mobility of doubly bound units which further limits their availability for reaction (Formula 1)



most common type of resorcinol/formaldehyde "tetramer"

Formula 1

The absence of methylol ($-CH_2OH$) groups in all six lower-molecular-weight RF condensates which have been isolated [4] reflects the high reactivity of resorcinol under acid or alkaline conditions. It also shows the instability of its para-hydroxybenzyl alcohol groups and their rapid conversion to para-hydroxybenzyl carbonium ions or quinone methides. This explains how identical condensation products are obtained under acid or alkaline reaction conditions [4]. In acid reaction conditions methylene ether-linked condensates are also formed, but they are highly unstable and decompose to form stable methylene links in 0.25 to 1 h at ambient temperature [6,7].

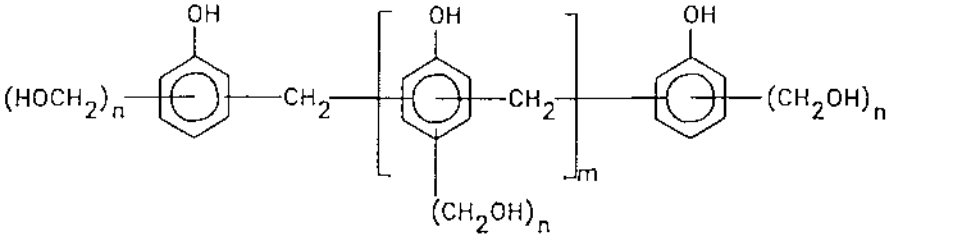
From a kinetic point of view, the initial reaction of condensation to form dimers is much faster than the subsequent condensation of these dimers and higher polymers. The condensation reaction of resorcinol with formaldehyde, on an equal molar basis and under

Copyright © 2003 by Taylor & Francis Group, LLC

identical conditions, also proceeds at a rate which is approximately 10 to 15 times faster than that of the equivalent PF system [8]. The high reactivity of the RF system renders it impossible to have these adhesives in resol form. Therefore, only RF novolaks, thus resins not containing methylol groups can be produced. Thus all the resorcinol nuclei are linked together through methylene bridges with no methylol groups being present and generally without any presence of methylene–ether bridges either.

The reaction rate of resorcinol with formaldehyde is dependent on the molar ratio of the two constituents, the concentration of the solution, pH, temperature, presence of various catalysts, and amount of certain types of alcohols present [9–12]. The effect of pH and temperature on the reactivity and gel time of the RF system presents the same trend as for all phenolic–formaldehyde reactions, with a minimum of reactivity at around pH 4 and the rate of reaction becoming rapidly faster at progressively more alkaline and more acid pH values [12,13]. Methanol and ethanol slow down the rate of reaction. Other alcohols behave similarly, the extent of their effect being dependent on their structure. Methanol lengthens gel time more than other alcohols, higher alcohols being less effective. The retarding effect on the reaction is due to temporary formation of hemiacetals between the methanol (or other alcohols) and the formaldehyde. This reduces the reaction rate because of the lower concentration of available formaldehyde [10,11]. Other solvents also affect the rate of reaction by forming complexes or by hydrogen bonding with the resorcinol [10,13].

In the manufacture of pure resorcinol resins the reaction would be violently exothermic unless controlled by the addition of alcohols. Because the alcohols perform other useful functions in the glue mix, they are left in the liquid glue. PRF adhesives are generally prepared firstly by reaction of phenol with formaldehyde to form a PF resol polymer that has been proved to be in the greatest percentage, and often completely, linear [4]. This can be represented as follows (Formula 2)

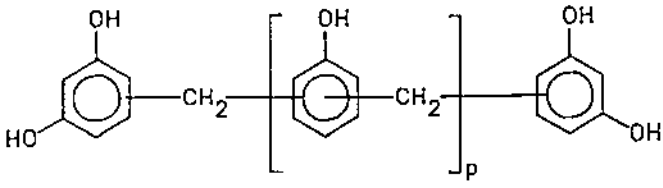


Formula 2

In the reaction that follows the resorcinol chemical is added in excess, in a suitable manner, to polymer I to react with the $-CH_2OH$ groups to form PRF polymers in which the terminal resorcinol groups can be a resorcinol or any type of RF polymer (Formula 3).

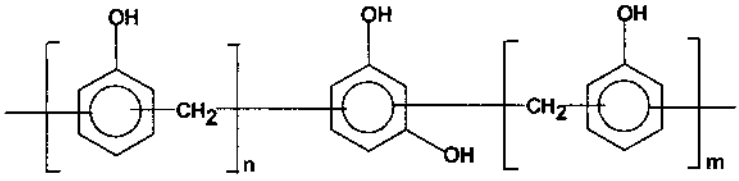
In reality, as resorcinol is expensive, the resin manufacturers tend to limit the amount of resorcinol grafted onto the PF resol. This is then generally lower than what is necessary to form structures as shown in Formula 3. Structures as these do occur but the majority of the polymers present in the PRF resin are of the type (Formula 4)

Copyright © 2003 by Taylor & Francis Group, LLC



p > 1 in integer numbers

Formula 3



with n and m > 1 and an integer number

Formula 4

where the residual third reactive site of the resorcinol is still free and is the site through which cross-linking takes place by reaction with the added formaldehyde hardener (see Chapter 8, Fig.1).

Where straight resorcinol adhesives are not suitable, resins can be prepared from modified resorcinol [13]. Characteristic of these types of resins are those used for tire cord adhesives, in which a pure RF resin is used, or alternatively, alkyl resorcinol or oil-soluble resins suitable for rubber compounding are obtained by prereaction of resorcinol with fatty acids in the presence of sulfuric acid at high temperature followed by reaction with formaldehyde. Worldwide more than 90% of resorcinol adhesives are used as cold-setting wood adhesives. The other most notable application is as tire cord adhesives, which constitutes less than 10% of the total use.

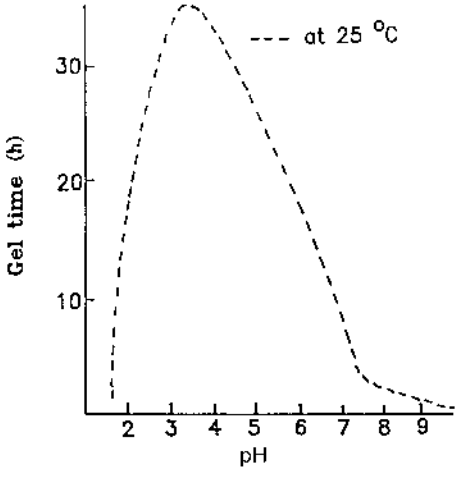


Figure 1 Effect of pH and temperature on the reactivity of the resorcinol–formaldehyde system.

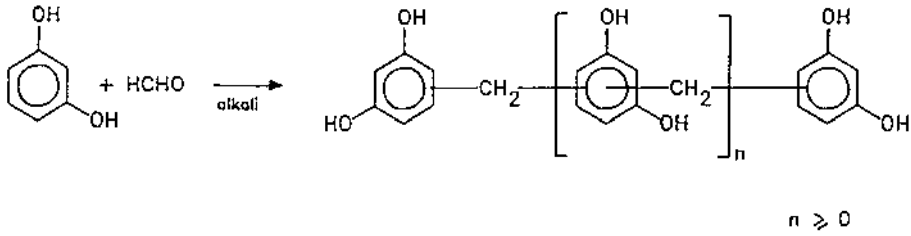
Copyright © 2003 by Taylor & Francis Group, LLC

III. WOOD LAMINATING AND FINGERJOINTING ADHESIVES

Various adhesive formulations can be used for the manufacture of laminated wooden beams and fingerjoints for structural purposes. Only those adhesive formulations that at some time or other have been used in industrial applications will be described. All these formulations are based totally or partially on resorcinol, and the hardening process is carried out at ambient temperature, to 50°C [14].

A. Adhesive 1: Resorcinol–Formaldehyde Adhesive

A RF novolak is produced according to the following schematic reaction (Formula 5):



Formula 5

If paraformaldehyde and fillers, generally wood and nutshell flours, are added, the resin becomes capable of setting in 2 to 3 h and curing in 16 to 24 h at ambient temperature.

B. Adhesive 2: Phenol–Resorcinol–Formaldehyde Adhesive and Powder, Liquid, or Sludge Hardener

A PF resol is prepared and resorcinol is grafted onto it according to the schematic reaction shown in Formula 6.

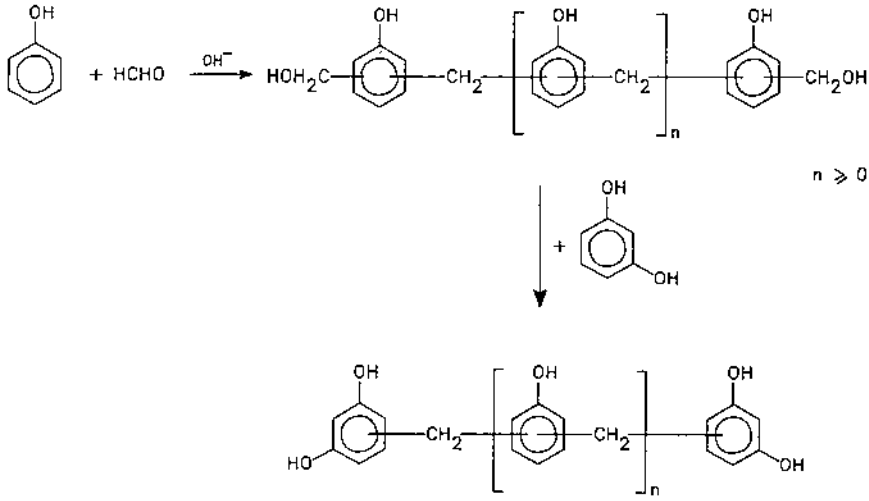
The resin produced is capable of setting in 2 to 3 h and cures in 16 to 24 h at ambient temperature once paraformaldehyde and wood and nut flour fillers have been added. This is the most commercially used type of resorcinol cold-set adhesive, variations on the theme concerning mainly the hardener. Thus, sometime and especially in Europe, sludges formed by suspensions of organic or inorganic fillers in water mixed with liquid hardeners such as formalin and urea–formaldehyde precursor concentrates are used as hardeners for this type of adhesive. As these sludges and liquid hardeners have a bad formaldehyde odor during usage, hardeners based on odorless oxazolidines are often used instead of formaldehyde-based ones in these liquid or sludge hardeners.

C. Adhesive 3: Urea–Resorcinol–Formaldehyde Adhesive

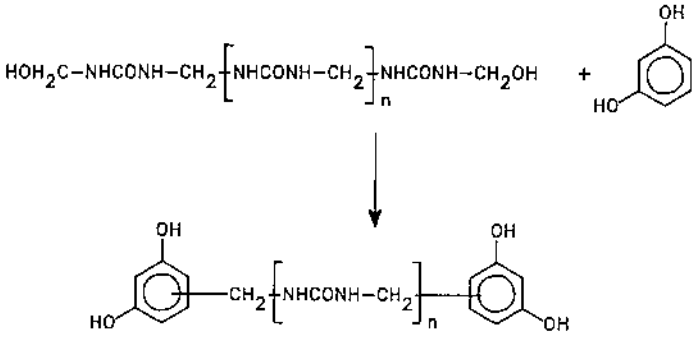
A urea–formaldehyde resin is prepared and resorcinol is grafted onto it as both terminal units or as middle connecting units leaving each resorcinol to present one or two still reactive sites through which to effect the final cross-linking and hardening of the resin. The schematic reaction is shown in Formula 7.

The behavior of this adhesive is identical to that of adhesive 2, although larger amounts of resorcinol are used. These adhesives have a higher formaldehyde/urea ratio,

Copyright © 2003 by Taylor & Francis Group, LLC



Formula 6



Formula 7

are water resistant, and are capable of radiofrequency curing. They can also be used for plywood manufacture, although the high price of resorcinol renders them unsuitable for such an application.

D. Adhesive 4: Phenol–Resorcinol–Formaldehyde and Liquid Hardener

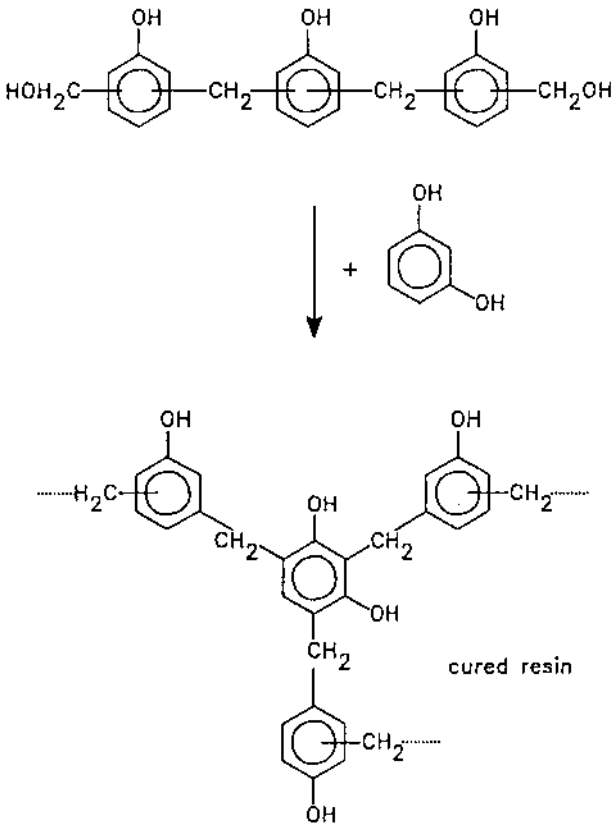
A PF resol is prepared which constitutes the resin. Resorcinol chemicals or RF novolaks, in aqueous or water–alcohol solutions, are used as hardeners according to the scheme in Formula 8.

E. Adhesive 5: Phenol–Resorcinol–Formaldehyde and Liquid Hardener

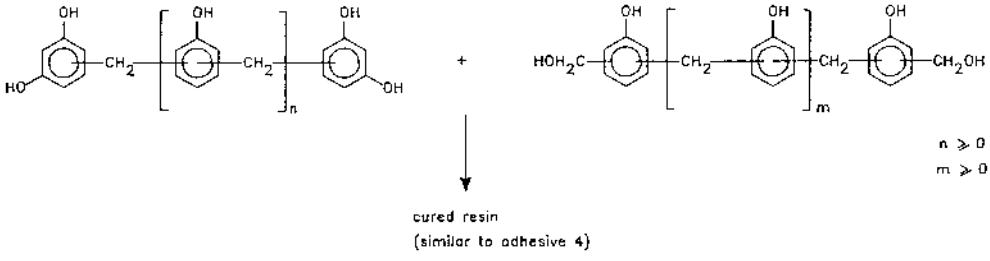
A PRF similar to adhesive 2 is prepared and a PF resol of the same type as adhesive 4 is used as a hardener. The schematic curing reaction is shown in the Formula 9.

The PRF adhesives are always delivered as a liquid and must be blended with a hardener before use. PRF adhesives of type 2 in which a liquid PRF adhesive is mixed with a powder hardener have been the most commonly used industrial systems, although in

Copyright © 2003 by Taylor & Francis Group, LLC



Formula 8



Formula 9

Europe the use of sludge hardeners of type 2 above is fairly common too. When using a powder hardener in adhesives of types 1, 2, and 3, they are mixed before use in a mass/mass ratio of liquid adhesive resin (50–60% solid content) to powder hardener of 5:1. The powder hardener is generally a mixture of 10 parts paraformaldehyde and 10% fillers. It is comprised of 200-mesh wood flour or a mixture of wood flour and nutshell flour, also 200 mesh. Adhesives of types 4 and 5 have a liquid resin to liquid hardener ratio of 1:1 by mass. This is so because the hardener is also a resin. Adhesives of types 4 and 5 have been used quite extensively in the past in certain markets but have now been superseded by adhesives of type 2 which have several handling advantages.

Copyright © 2003 by Taylor & Francis Group, LLC

Adhesives of type 3, although good, have not really caught on commercially and were developed as an alternative to PRFs of type 2 due to the ever increasing price of oil-derived phenol. In this regard adhesives of type 2 in which the phenol has been completely substituted by a flavonoid tannin have also been developed and have been used commercially in a few southern hemisphere countries for more than 30 years now. Their preparation and performance is detailed in the tannin adhesives chapter (Chap. 27). Pure RF adhesives (type 1) were used extensively earlier (until some 25–35 years ago). They fell into disfavor because of the high price of the resorcinol chemical needed to make them and also due to the shortage of resorcinol supply in 1960 and 1970 (oil crises). They are still used in some industrial applications, particularly at low temperature curing and when difficult wood-gluing problems arise, but they constitute less than 1% of the total market by volume, except in tire cord adhesives which consume in general between 1 and 12% of the resorcinol produced in the world (hence about one sixth of the amount used for wood adhesives). PRF adhesives together with liquid hardeners are used quite extensively in Europe, as they have several handling advantages for this market. These adhesives are mixed before use in a mass/mass ratio of adhesive to liquid hardener from 5 : 1 to 2.5 : 1 of even 1 : 1 (depending on the type). The powder hardener is generally a mixture of equal parts paraformaldehyde fine powder and fillers, these latter comprising 200-mesh wood flour or a mixture of wood flour and nutshell flour, 200–300 mesh. Adhesive types presenting a liquid hardener use as hardeners formaldehyde, paraformaldehyde, formurea, and, when necessary to avoid undue formaldehyde smell, oxazolidine. In addition these hardeners also contain fillers and thickening agents.

All properly formulated resorcinol-based adhesives must have a viscosity low enough in aqueous alcoholic solutions to flow with ease into all the interstices of the wood surface. Wetting ability is promoted by the alcohol. The paraformaldehyde used as a hardener in powder hardener types is an addition polymer composed of a few to over 100 formaldehyde monomers. It dissolves slowly in water, by depolymerization to formaldehyde monomers. The rate of depolymerization depends on the degree of polymerization of the paraformaldehyde, the size of the particles, and the pH. Therefore, the working life or pot life of a glue mix can be adjusted by selecting the type of paraformaldehyde and the pH correctly, but the ratio of resorcinol to phenol will also have an influence on the pH value to be chosen. Fillers are added to give consistency to the glue mix, to control viscosity and thixotropic characteristics, to form a fibrous reinforcement of the adhesive film, and to lessen the cost. Wood flour is used as a filler to obtain better gap filling properties where rough or uneven surfaces must be bonded, or where low bonding pressures must be used. Nutshell flours, such as coconut shell flour, walnut shell flour, peach pip shell flour, macadamia nut shell flour or even olive stone flour are used as fillers to provide smooth-flowing powder mixtures. Inorganic fillers are also used, especially in Europe, although this is a practice to avoid as it is very heavy on saws afterwards. Clays and fumed silica can also be used in very small amounts to control the thixotropic consistency of the glue mix.

As the formaldehyde reacts with the resorcinol-based resin, condensation occurs, with the formation of high-molecular-weight polymers. There is considerable secondary force interaction between the growing resorcinol polymers and the noncrystalline hemicellulosic and lignocellulosic molecules of the substrate. The highly polar methylol groups and the phenolic hydroxy groups link to cellulose and lignin groups by van der Waals, hydrogen, and electrostatic bonds. The growing adhesive polymers continue to interact to form colloidal particles and then a gelatinous film. This mechanism depends

Copyright © 2003 by Taylor & Francis Group, LLC

Table 1 Typical Tensile Strength and Percentage Wood Failure Results Obtainable with Synthetic PRF Resins[a]

	Dry test	24-h cold water soak	6-h boil test
Strength (N)	3000–3500	2600–3200	2500–3000
Wood failure (%)	90–100	75–100	75–100

[a]Tested according to Refs. 15 and 16.

strongly on the moisture content of the wood, which determines the rate of water and solvent absorption.

The advantage of ambient-temperature curing is that the moisture escapes gradually from the hard film formed on curing, inducing a minimum of residual stresses on the joint and allowing the glue line to assume the aspect of a molecularly porous solid. As a consequence, the hard film is able to transpire in the same way as wood, which minimizes checking or crazing and allows the glued joint to survive exposure to the extremes of humidity cycles. To shorten the curing time heating chambers (40–60°C) are often used in the manufacturing of glulam, and an even faster curing can be achieved with the use of radiofrequency curing presses. Typical levels of strength and wood failure results obtained in specific standard tests are shown in Table 1.

IV. SPECIAL ADHESIVES OF REDUCED RESORCINOL CONTENT

A. Fast-Setting Adhesive for Fingerjointing and Glulam

Together with the more traditional fingerjointing adhesives that have just been discussed, a series of ambient-temperature fast-setting separate application systems have also been developed. These eliminate the long delays caused by the use of more conventional PRF adhesives, which require lengthy periods to set. These types of resorcinol adhesives are applied separately. They were first developed in the United States [17–20] to bond large components where presses were impractical. Kreibich [20] describes these separate application or ''honeymoon'' systems as follows: ''Component A is a slow-reacting phenol-resorcinol-formaldehyde resin with a reactive hardener. Component B is a fast-reacting resin with a slow-reacting hardener. When A and B are mated, the reactive parts of the component react within minutes to form a joint which can be handled and processed further. Full curing of the slow-reacting part of the system takes place with time.'' The *m*-aminophenol used for component B is a frightfully expensive chemical and for this reason these systems were discarded and not used industrially [14]. In their original concept component A is a traditional PRF cold-setting adhesive at its standard pH of between 8 to 8.5 to which formaldehyde hardener has been added. Flour fillers may be added or omitted from the glue mix. Component B is a phenol/meta-aminophenol/formaldehyde resin with a very high pH (and therefore a high reactivity) which contains no hardener or only a very slow hardener.

More recently, a modification of the system described by Kreibich has been used extensively in industry with good success. Component A of the adhesive is again a standard PRF cold-setting adhesive with powder hardener added at its standard pH. Component B can be either the same PRF adhesive with no hardener and the pH adjusted to 12 or a 50 to 55% tannin extract solution at a pH of 12–13, provided that the tannin is

Copyright © 2003 by Taylor & Francis Group, LLC

of the condensed or flavonoid type, such as mimosa, quebracho or pine bark extract with no hardener [3, 21]. The results obtained with these two systems are good and the resin not only has all the advantages desired but also as a result of the use of vegetable tannins and of the halving of the resorcinol content of the entire adhesive system is considerably cheaper [3,21,22].

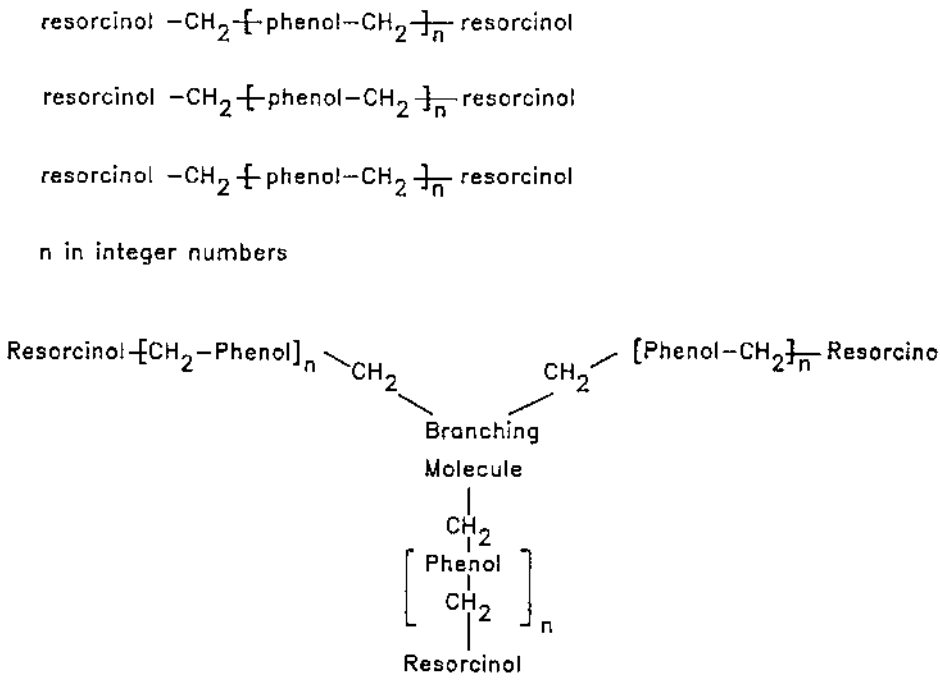
The adhesive works in the following manner. Once the component A glue mix is spread on one fingerjoint profile and component B on the other fingerjoint profile and the two profiles are joined under pressure, the reaction of component B with the hardener of part A is very fast. In 30 min at 25°C fingerjoints prepared with these adhesives generally reach the levels of strength that fingerjoints glued with more conventional phenolic adhesives are able to reach only after 6 h at 40 to 50°C or in 16 to 24 h at 25°C [3,22]. Clamping of laminated beams (glulam) bonded with these fast-set honeymoon adhesives is an average of only 3 h at ambient temperature compared with the 16 to 24 h necessary with traditional PRF resins [21,22]. These adhesives present also two other advantages, namely (i) they are able to bond without any decrease of performance at temperatures down to 5°C and (ii) they are able to bond "green" timber at high moisture content, a feat which has been used in industrial glulam bonding since their commercial introduction in 1981. Several variations on the theme exist, such as the "Greenweld" system from New Zealand in which component B is a solution composed of just ammonia as a strong accelerator of the PRF plus hardener of component A, and of a thickener; this system, however, suffers from the presence of the odor of ammonia which is unacceptable in some sophisticated markets.

B. Branched PRF Adhesives

Recently another step forward has been taken in the formulation of PRF adhesives of lower resorcinol content. Liquid resorcinol or PRF resins appear to be mostly linear [4]. The original concept in "branching" erroneously maintained that if a chemical molecule capable of extensively branching (three or more effective reaction sites with an aldehyde) is used after, before, or during, but particularly during or after, the preparation of the PF resin, the polymer in the branched PRF adhesive has (1) higher molecular weight than in normal PRF adhesives where branching is not present and (2) higher viscosity in water or water/solvent solutions of the same composition and of the same resin solids content (concentration). It also needs a much lower resorcinol amount on the total phenol to present the same performance as normal linear PRF adhesives. This can be explained schematically and is shown in Formula 10. With $n \geq 1$ and an integer number and comparable to, similar to, or equal to n in formula 9 for the production of PRF resins.

When comparing linear and branched resins, for every n molecules of phenol used a minimum of 2 molecules of resorcinol are used in the case of a normal, traditional linear PRF adhesive, whereas only 1 molecule of resorcinol for n molecules of phenol is used in the case of a "branched" PRF adhesive. The amount of resorcinol has then been halved or approximately halved in the case of the branched PRF resin. A second effect caused by the branching is a noticeable increase in the degree of polymerization of the resin. This causes a considerable increase in the viscosity of the liquid adhesive solution. Because PRF adhesives must be used within fairly narrow viscosity limits, to return the viscosity of the liquid PRF adhesive to within these limits, the resin solids content in the adhesive must be lowered considerably, with a consequent further decrease in the total liquid resin of the amount of resorcinol and of the other materials, except solvents and

Copyright © 2003 by Taylor & Francis Group, LLC



Formula 10

water. This decreases the cost of the resin further without decreasing its performance. Thus, to conclude, the decrease in resorcinol by branching of the resin is based on two effects:

1. A decrease in resorcinol percentage in the polymer itself, hence in the resin solids, due to the decrease in the number of the PF terminal sites onto which resorcinol is grafted during PRF manufacture.
2. An increase in molecular weight of the resin, which by the need to decrease the percentage of resin solids content to a workable viscosity decreases the percentage of resorcinol on liquid resin (not on resin solids).

It is clear that in a certain sense a branched PRF will behave as a more advanced, almost precured phenolic resin. While the first effect described is a definite advance on the road to better engineered PRF resins, the second effect can also be obtained with more advanced (reactionwise) linear resins. The contribution of the second effect to the decrease in resorcinol is not less marked than that of the first effect. It is, however, the second effect that accounts for the difference in behavior between branched and linear PRF adhesives.

Branching molecules which can be used could be resorcinol, melamine, urea and others [23]. Urea is the favorite one, because it is much cheaper than the others and needs to be added in only 1.5 to 2% of total resin. When urea is used as a brancher, the adhesive assumes an intense and unusual (for resorcinol resins) blue color, after a few days, hence its nickname, ''blueglue.'' However, later work [24,25] has shown that tridimensional branching has very little to do with the improved performance of these low-resorcinol content adhesives, with tridimensionally branched molecules contributing, at best, no more than 8 to 9% of the total strength [24,25]. In reality, addition of urea causes the

Copyright © 2003 by Taylor & Francis Group, LLC

reaction as foreseen, but not in three points of branching but rather only in two sites of the branching molecule. This is equivalent to saying that most of the resin doubles linearly in molecular weight and degree of polymerization, while the final effect, good performance at half the resin resorcinol content, is maintained [24,25]. This effect is based on the relative reactivity towards phenolic methylols of urea and of unreacted phenol sites and thus while the macro effect is as wanted, at the molecular level it is only a kinetic effect due to the different relative reactivities of urea and phenol under the reaction conditions used. Thus

$$\text{resorcinol}-\text{CH}_2\text{-}[\text{-phenol}-\text{CH}_2]_n\text{-resorcinol}$$

$$\text{resorcinol}-\text{CH}_2\text{-}[\text{-phenol}-\text{CH}_2]_n\text{-resorcinol}$$

$$\downarrow$$

$$\text{resorcinol}-\text{CH}_2\text{-}[\text{-phenol}-\text{CH}_2]_n\text{-urea}-\text{CH}_2 + \text{phenol}-\text{CH}_2]_n\text{-resorcinol}$$

halving of the resorcinol content is still obtained, but between 90 and 100% of the polymers in the resin are still linear. It is noticeable that the same degree of polymerization and "doubling" effect cannot be obtained by lengthening the reaction time of a PF resin without urea addition [24,25].

These liquid resins then work at a resorcinol content of only 9 to 11%, hence considerably lower than that of traditional PRF resins. These resins can also be used with good results for honeymoon fast-setting adhesives in PRF–tannin systems, thus further decreasing the total content of resorcinol in the total resin system at a level as low as 5 to 6%.

C. Cold-Setting PF Adhesives Containing no Resorcinol

As the cost of cold-setting exterior-grade adhesives based on resorcinol is very high due to the high cost of resorcinol itself, the tendency to decrease the amount of resorcinol while maintaining unaltered the performance of the adhesive, when brought to its ultimate conclusion leads to the concept of exterior cold-setting phenolic adhesives of zero level resorcinol. As alkaline PF resins do not have an ambient temperature rate of reaction that is even vaguely sufficient to set and harden the adhesive to a sufficient level, some modifications need to be introduced to overcome in this regard the lack of resorcinol. This can be done in several ways: (i) by using standard PF thermosetting resol resins and hardening them by increasing the glue line temperature by radiofrequency in fingerjointing and glulam manufacture. The system is expensive and needs considerably higher capital outlay and more careful handling of both the equipment and of the joint, for results that are certainly not particularly exciting. (ii) By using resins in which the PF resol of adhesives of type 2 above is terminated by the terminal grafting of a resorcinol substitute, for example a natural polyflavonoid tannin [26], this system being truly cold setting and yielding relatively good results but at best just on the inferior limit of the standard requirements [26]. (iii) By using self-neutralizing acid-setting PF resols. The term "acid-setting" when used in the presence of a lignocellulosic substrate makes wood technologists shudder, conjuring visions of extensive acid-induced substrate degradation and early exterior joint failure. And this is indeed the case! In reality some exterior aminoplastic resins do harden in the moderately acid range without any major substrate degradation problems. PF resins, however, while hardening very rapidly under acid conditions, do need very acid conditions to give a hardened strong network, and this elevated acidity is not really acceptable as regards long term durability of the substrate. The damage due to the acid hydrolysis of

Copyright © 2003 by Taylor & Francis Group, LLC

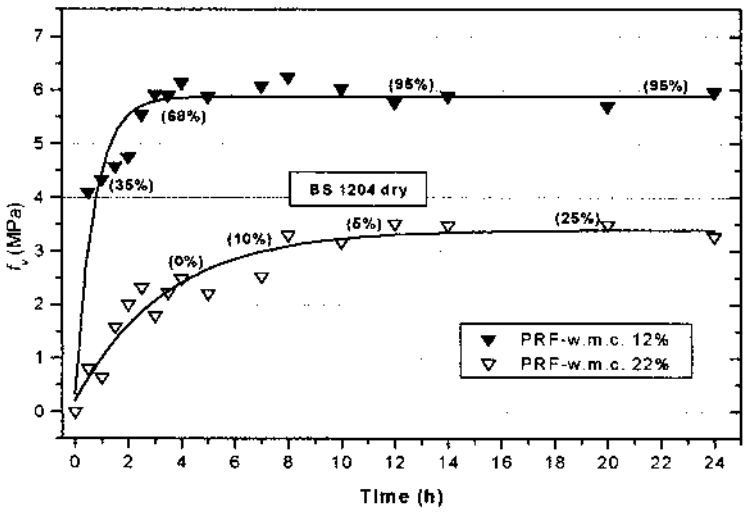


Figure 2 Typical strength and wood failure increase as a function of time of a pure PRF honeymoon adhesive system on timber at 12% and 22% moisture content [26–29]. Note that at the unusually high moisture content of 22% the requirements of the standards are passed in less than 24 h as the timber starts to dry [26–29]. Test on beech strips according to British Standard BS 1204.

cellulose and other wood carbohydrates is particularly aggravated and compounded by the long term effect of the glue line remaining acid after resin hardening. However, the main negative effect due to acid-induced degradation of the substrate has been overcome by using acid-setting PF resins containing no resorcinol but hardened by the use of a self-neutralizing catalyst [27]. According to this principle the adhesive first becomes acid to allow the PF resin to cure and after hardening the hardened glue line self-neutralizes in very short time [27]. The greater majority of the effects of substrate degradation are then avoided and very strong and durable exterior wood joints are produced [27]. The system works well in radiofrequency cured joints, yielding much better results than the alkaline resols of point (i) above, and can work well under purely cold-setting conditions [27] (Fig. 2).

Other rapid setting adhesive systems not containing resorcinol are those based on melamine–urea–formaldehyde resins and on one-component polyurethanes, described in Chap. 32 and Chap. 34, respectively [28,29].

V. FORMULATION FOR ADHESIVES OF TYPE 2 [14]

A basic formulation capable of giving more than adequate results is presented here so that a starter in the field can get aquainted with these types of adhesives. The procedure for the preparation of this resin can be modified in many ways by varying catalysts, concentration, molar ratios, and condensation conditions.

Phenol, 110 parts by mass + 22 parts water
First formalin 37% solution, 49 parts by mass
H_2SO_4 10% solution, 22 parts by mass
First NaOH 40% solution, 4.5 parts by mass

Copyright © 2003 by Taylor & Francis Group, LLC

Second NaOH 40% solution, 9.25 parts by mass
Second formalin 37% solution, 90 to 93 parts by mass
Methanol or methylated spirits, 30 parts by mass (at start of reaction)
Resorcinol, 71 parts by mass
Tannin extract, 19 parts by mass (only as a thickener: another thickener can also be used as soon as it is not excessively sensitive to water attack).

Phenol, water, methanol, and the first amount of formalin solution are charged in the reaction vessel and heated mildly until the phenol is dissolved. H_2SO_4 is added and the temperature increased to reflux under continuous mechanical stirring. The mixture is refluxed for 3.5 to 4 h (generally ± 4 h) under continuous mechanical stirring. It is cooled to 50 to 60°C and the following is added: the two amounts of NaOH 40% solution (slowly) and the second amount of formalin solution while maintaining the mix under continuous mechanical stirring. The mixture is then refluxed for 4.5 to 4.75 h and then the resorcinol added. The mixture is refluxed for a further 30 to 50 min. Spray-dried mimosa tannin extract is added immediately before or during cooling to adjust the viscosity to the wanted level; the pH must be adjusted to 8.5 to 9.5 according to the pot life required. The reaction must be carried out under continuous mechanical stirring throughout the whole reaction period. The hardener is a 50 : 50 mixture of paraformaldehyde 96% (usually a fast grade) fine powder and 180- to 200-mesh softwood flour (60 : 40 mass proportion) which is added to the liquid resin generally in the proportions by mass of liquid resin: powder hardener = 100 : 20 to 100 : 25.

REFERENCES

1. J. M. Dinwoodie, in *Wood Adhesives Chemistry and Technology*, Vol. 1 (A. Pizzi, ed.), Marcel Dekker, New York, 1983, pp. 1–58.
2. R. E. Kreibich, in *Wood Adhesives*: *Present and Future* (A. Pizzi, ed.), Applied Polymer Symposium 40, 1984, pp. 1–18.
3. A. Pizzi, D. du T. Rossouw, W. Knuffel and M. Singmin, *Holzforsch. Holiverwert. 32*(6): 140 (1980).
4. A. Pizzi, R.M. Horak, D. Ferreira, and D.G. Roux, *Cell*, *Chem. Technol. 13*: 753 (1979).
5. R. A. V. Raff and B. M. Silverman, *Ind. Eng. Chem. 43*: 1423 (1951).
6. D. du T. Rossouw, A. Pizzi, and G. McGillivray, *J. Polymer Sci. Chem. Ed. 18*: 3323 (1980).
7. A. Pizzi and P. van der Spuy, *J. Polymer Sci. Chem. Ed. 18*: 3477 (1980).
8. G. G. Marra, *Forest Prod. J. 6*: 97 (1956).
9. R. A. V. Raff and B. H. Silverman, *Can. Chem. 29*: 857 (1951).
10. A. R. Ingram, *Can. Chem. 29*: 863 (1951).
11. C. T. Liu and T. Naratsuka, *Mokuzai Gakkaishi 15*: 79 (1969).
12. P. H. Rhodes, *Mod. Plastics 24*(2): 145 (1947).
13. R. H. Moult, in *Handbook of Adhesives*, 2nd ed. (I. Skeist, ed.), Reinhold, New York, 1977, pp. 417–423.
14. A. Pizzi, in *Wood Adhesives Chemistry and Technology*, Vol. 1 (A. Pizzi, ed.), Marcel Dekker, New York, 1983, pp. 105–178.
15. Specification for synthetic resin adhesives for wood, Part 2; Close contact joints, British Standard BS 1204, 1965.
16. Standard specification for phenolic and aminoplastic adhesives for laminating and fingerjointing of timber, and for furniture and joinery, *SABS 1349-1981*, South African Bureau of Standards, 1981.
17. G. F. Baxter and R. E. Kreibich, *Forest Prod. J. 23*(1): 17 (1973).

Copyright © 2003 by Taylor & Francis Group, LLC

18. R. W. Caster, *Forest Prod. J. 23*(1): 26 (1973).
19. H. Ericson, *Papper Tra 1*: 19 (1975).
20. R. E. Kreibich, *Adhesives Age 17*: 26 (1974).
21. A. Pizzi and F. A. Cameron, *Forest Prod. J. 34*(9): 61 (1984).
22. A. Pizzi and F. A. Cameron, in *Wood Adhesives Chemistry and Technology*, Vol. 2 (A. Pizzi, ed.), Marcel Dekker, New York, 1989, pp. 229–306.
23. A. Pizzi, in *Wood Adhesives Chemistry and Technology*, Vol. 2 (A. Pizzi, ed.), Marcel Dekker, New York, 1989, pp. 190–210.
24. E. Scopelitis, M.Sc. thesis, University of the Witwatersrand, Johannesburg, South Africa, 1992.
25. E. Scopelitis and A. Pizzi, *J. Appl. Polymer Sci. 47*: 351 (1993); *48*: 2135 (1993).
26. A. Pizzi, F. A. Cameron, and E. Orovan, *Holz Roh Werkstoff 46*: 67 (1988).
27. A. Pizzi, R. Vosloo, F. A. Cameron, and E. Orovan. *Holz Roh Werkstoff 44*: 229 (1986).
28. M. Properzi, A. Pizzi, and L. Uzielli, *Holz Roh Werkstoff 59*: 413 (2001).
29. M. Properzi, A. Pizzi, and L. Uzielli, *Holzforschung Holzverwertung 53* (4): 114 (2001).

Copyright © 2003 by Taylor & Francis Group, LLC